Oxygen Barrier Efficiency of Hexamethyldisiloxane/Oxygen Plasma-Deposited Coating

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SYNOPSIS

Oxygen barrier coatings were made by plasma polymer deposition on a polypropylene substrate. Plasma polymer deposition is realized in a low-frequency reactor with hexamethyldisiloxane/oxygen (HMDSO/O$_2$) precursors. The structure and composition of the deposited coating are characterized by density measurements and FTIR spectroscopy. Permeability of the polypropylene, coated with plasma films made from various gas compositions, is interpreted in terms of coating structure and composition. Incorporation of molecular oxygen in the gas phase results in inorganic and dense films. It is shown that the density of the film is the main factor controlling the oxygen barrier effect. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The chemical composition and structure of plasma-deposited materials strongly depend on deposition parameters[1,2] and gas composition. This technique produces plasma polymers whose properties are different from conventional polymers and permit depositions on substrates made from different materials (polymers, glasses, metals, etc.). Thus, one can obtain thin uniform films, pinhole free, whose properties are used in various areas such as the separation of gases,[3,4] anticorrosion coatings,[5] or barrier coatings for gases[6] in packaging. Studies have been carried out on the formation of plasma polymer membranes and on the modification of the polymer properties by surface processing.[2,7] As for conventional polymeric membranes, the study of gas permeability can be divided into two parts: the sorption of deposited films[2] and the modification of the sorption of a polymer membrane under the plasma effect,[7] the second part being the diffusion of gases through the plasma polymer.[8] Most of the studies concerned the permeability of composite membranes formed by a plasma-deposited coating on a polymer substrate.[7,9,10]

Plasma polymers provide excellent gas barrier films due to their three-dimensional structures rather than to linear chains, resulting in the low mobility of chain segments.[2] Also, the density of a plasma film is generally higher than that of an equivalent material made by using more conventional ways.[1,11] Moreover, their compositions are easily adjustable by the control of plasma parameters and the gas composition. It was shown that SiO$_x$ thin films gave good results as oxygen barriers.[6,12] Hence, organosilicon precursors were used for this purpose. There are several ways to obtain the SiO$_x$ structure with this kind of precursor. One can use an oxygen plasma postdeposition treatment on hexamethyldisiloxane (HMDSO) films to eliminate the organic part in the first few monolayers.[13] Another way is the ablation of the organic part during the deposition process. This is achieved by using an HMDSO/oxygen mixture plasma. The aim of this article was to evaluate the oxygen barrier properties of such plasma films and to understand the main factors controlling the barrier effect. For pure HMDSO plasma, the injected power,[11] the substrate temperature,[5] and the oxygen contents in the gas phase can change drastically the composition of the deposited film. In fact, it is quite easy to obtain an almost perfectly inorganic film or, if required, a film exhibiting a large content of organic groups. HMDSO/O$_2$ mixture plasma films were deposited

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on polypropylene substrates, keeping all parameters except the gas-phase composition as constant. Although the details of the mechanisms are not very clear, most of the authors agree that increasing the oxygen concentration in the gas phase leads to the reduction of the organic groups in the films. Fourier transform infrared analysis (FTIR) and density measurements give information on the structure and composition of plasma films. They have been analyzed in the light of their oxygen barrier properties.

EXPERIMENTAL

The reactor used for these experiments consists of two parallel-plate electrodes, 6 cm in diameter, in a cylindrical bell jar. The high-voltage electrode is connected via a capacitor to a 2.5 kHz power supply. The substrate is a polypropylene (PP) film, 20 μm thick, placed on the power electrode. The pressure in the reactor was reduced to approximately 10^{-3} mbar before the gas mixture was introduced through needle valves, elevating the total working pressure to 10^{-1} mbar. The electrical power density used in this work was 100 mW/cm^2, and the deposition time, 10 min. Pressure, power and deposition time were the same for all the results presented here.

Film densities were determined using a quartz balance, Plassys IL 150. Usually, this system is used to control the thickness of a deposit assuming a known density. In our experiments, the oscillation frequency is measured before deposition. Then, the quartz sensor is placed in the reactor in such a way that the same deposit occurs on the quartz sensor and on the polypropylene substrate. This last assumption has been checked for a given film thickness. Then, the new oscillation frequency is measured. A part of the surface of the quartz sensor is protected during the deposition in order to provide a way to measure the thickness of the deposit using a talystep. From the oscillation frequency shift, thickness, and surface of the deposit on the quartz sensor, it is possible to estimate the density. However, a relatively large error remains possible especially for lower thicknesses due to the lack of accuracy in the thickness measurements. So, we will go back to the limitations of this procedure in the discussion.

Permeability to oxygen was measured at room temperature using a laboratory test consisting of a cell separated into two parts by the membrane under experiment and a gas-phase chromatographer. Both parts of the cell were first subjected to a helium gas flow in order to remove all contaminants. Then, ox-

ygen was introduced into the upper part and helium (vector gas of the chromatography) in the lower part in an identical manner at the same time. Thereafter, the gas supply was cut off and the cell was isolated from the rest. Both gases were now at the same pressure (2 bars) with the membrane in between. The diffusion of oxygen across the membrane takes place due to the driving force resulting from the oxygen-pressure difference across it. After a certain time, the gas contained in the lower part of the cell was analyzed using gas chromatography and the oxygen diffused through the membrane appeared as a peak on the recorder (Hewlett-Packard 3396 series II integrator). The peak area is related to the quantity of oxygen diffused during the experiment. Thus, the oxygen flow can be easily calculated as a function of the peak area using a simple calibration.

A Biorad FTS 60 A IR spectrometer was used for FTIR measurements on silicon substrates. These silicon substrates are placed on a polypropylene sample during plasma deposition. Hence, identical deposits take place on silicon and polypropylene substrates.

RESULTS AND DISCUSSION

1. Oxygen flow through the membranes is expressed in terms of the gas flow through the uncoated polypropylene substrate (600 cm^3/ m^2 day being the reference value). Barrier qualities of the membranes are satisfactory since the measured flows are lower than 3% of the reference value as shown in Figure 1. This figure also shows that the permeability depends to a great extent on the oxygen content of the plasma phase and becomes minimum when it exceeds 50%.

2. The density of the conventional polysiloxanes is typically 0.97 g/cm^3. Plasma polysiloxanes, obtained from HMDSO without the addition of oxygen in the gas phase, have a slightly higher density. This result was expected because of the particular method of polymerization. The densities range between 1 and 2 g/cm^3 depending on the deposition parameters and plasma conditions.[11,13] Results reported in the present work show that the density of plasma films increases with oxygen content in the gas phase (1 g/cm^3 for pure HMDSO to 2.7 g/cm^3 with 80% of oxygen content). This last value, surprisingly high, is probably due to a relatively large uncer-
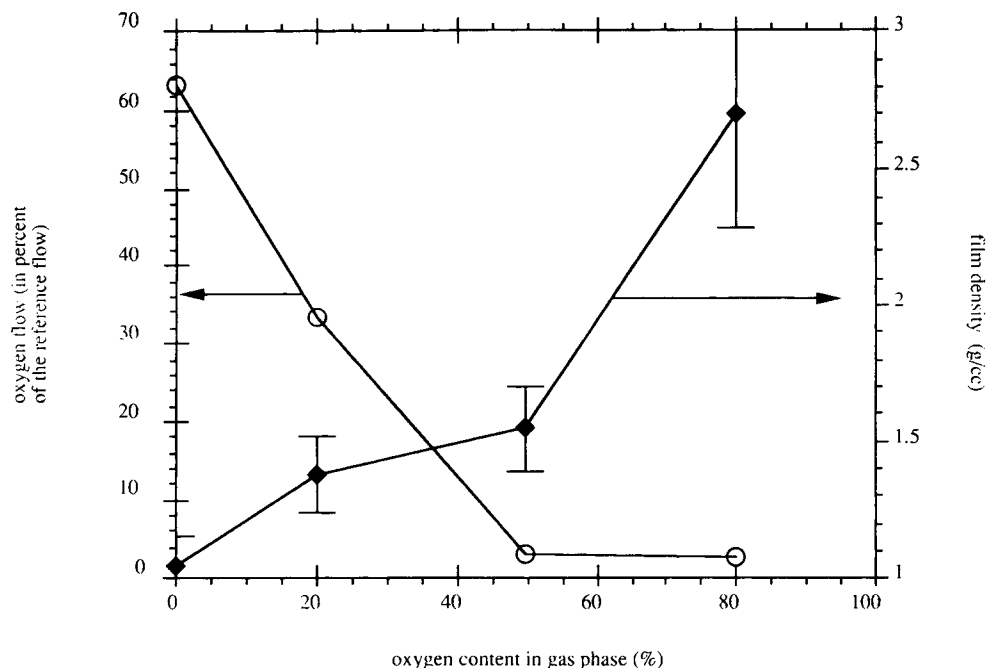
oxygen content in gas phase (%)

Figure 1 Oxygen flow across membranes and density of plasma polymer films (with errors bars due to thickness incertitude of deposits) for different gas-phase compositions. Uncoated polypropylene reference flow = 600 cm³/m² day. Initial gas total pressure = 10^{-1} mbar; power density = 100 mW/cm²; deposition time = 10 min.

tainty in determining the exact thickness especially for very thin layers.

3. Besides film density, a change in the oxygen percentage in the gas phase can also alter the film composition. Figure 2(a)-(c) shows typical infrared spectra of a plasma-deposited film. Assignments of the bands (Table I) have already been published.[14] For the purpose of this article, attention will be paid to the Si — O — Si band located between 1000 and 1150 cm⁻¹ and to the two Si — (CH₃) bands, located at 840 cm⁻¹ for the first [Si — (CH₃)₃] and 800 cm⁻¹ for the other [Si — (CH₃)₂]. The last two peaks are representatives of the organic part, and the first, the inorganic part of the plasma films. The ratio R of their areas (R = [SiOSi (1100 cm⁻¹) area]/[Si(CH₃)₃ (840 cm⁻¹) + Si(CH₃)₂ (800 cm⁻¹) area]) is given in Figure 3 as a function of the molecular oxygen content in the gas phase. There is a notable decrease of the organic part in the film beyond 20% of oxygen. The same results have been reported with organosilicon/oxygen mixtures for radio-frequency-deposited films[15] and microwave-deposited films.[16] Sometimes, confirmation of IR results have been obtained from

X-ray photoelectron spectroscopy (XPS) measurements, indicating that the organic part is less than 5% in the film when the oxygen content in the gas phase is higher than 80%.[16]

The curve in Figure 3 is similar to the curve shown for the film density in Figure 1. In both cases, the experimental parameter which varies is the oxygen content in the gas phase. Figures 1 and 3 indicate that both density and composition change with the oxygen content. The decay of permeability of oxygen molecules through the membranes can then be attributed to the increase in film density or/and to the change in their chemical composition. In the first case, the diffusion of molecular oxygen would be controlled by the "free volume" inside the plasma film and, in the latter case, by the sorption mechanism at the surface, i.e., the molecular interaction between the diffusing species and atoms of the deposited coating. This will be further explained later.

Another parameter has also been considered. As the oxygen content increases, the growth rate of the plasma film decreases. Consequently, in the results reported here, the thickness of films is not constant. Table II gives the values of thickness
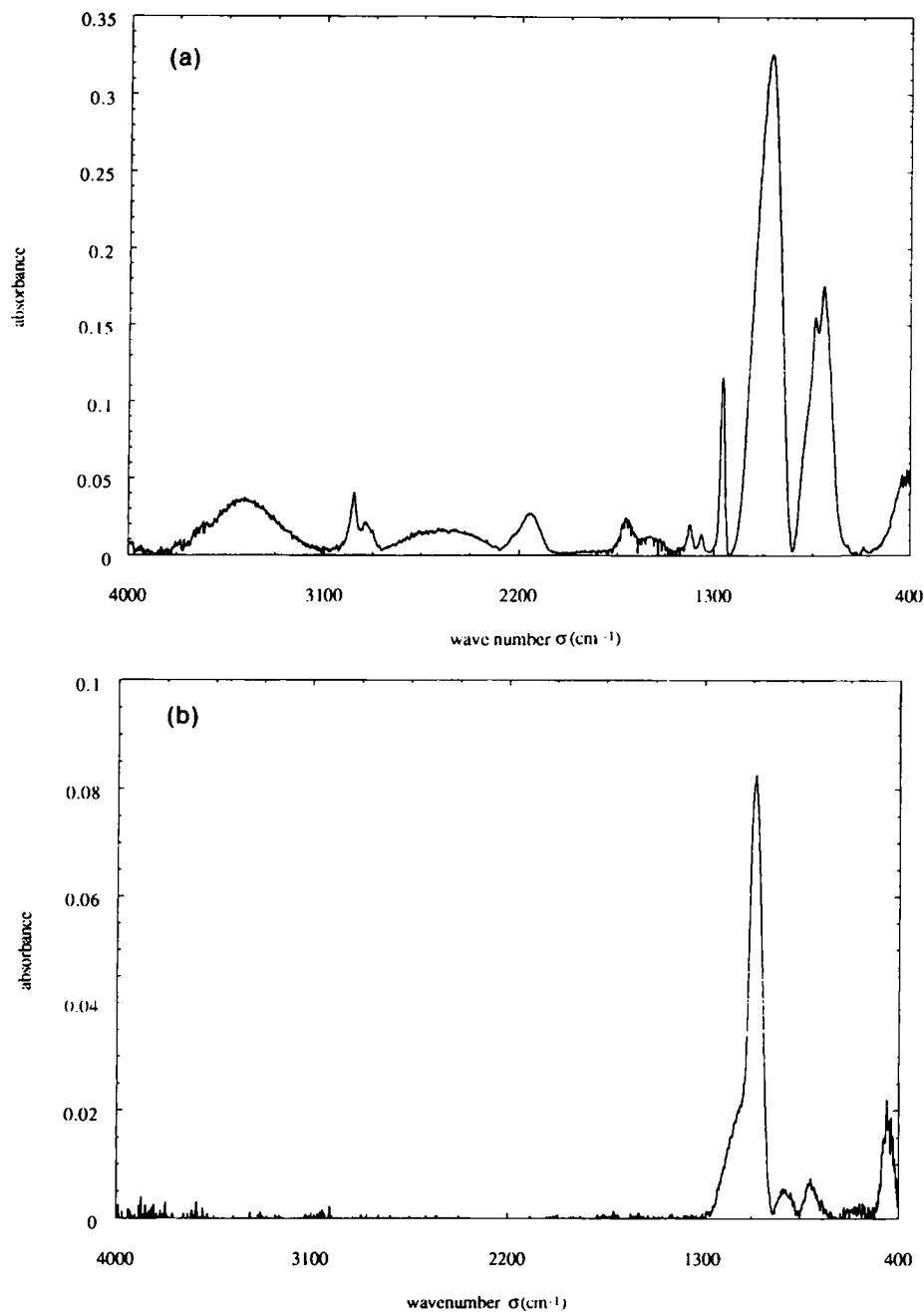
Figure 2 (a) Typical infrared spectra of pure HMDSO plasma-deposited film in 400–4000 cm^{-1} range. (b) Typical infrared spectra of HMDSO/O$_2$ (20% HMDSO, 80% O$_2$) plasma-deposited film in 400–4000 cm^{-1} range. (c) Typical infrared spectra of pure HMDSO plasma-deposited film in 600–1400 cm^{-1} range.

and permeability of films elaborated under different conditions. These values show that although the thickness of the coating decreases its barrier efficiency increases with the oxygen content in the gas phase.

The membrane permeability is expressed as a function of two parameters controlling the gas flow. First, the gas is sorbed at the surface of the polymer and then diffuses under the effect of the concentration gradient. Accordingly, the permeability coefficient, P, is given by the following expression:
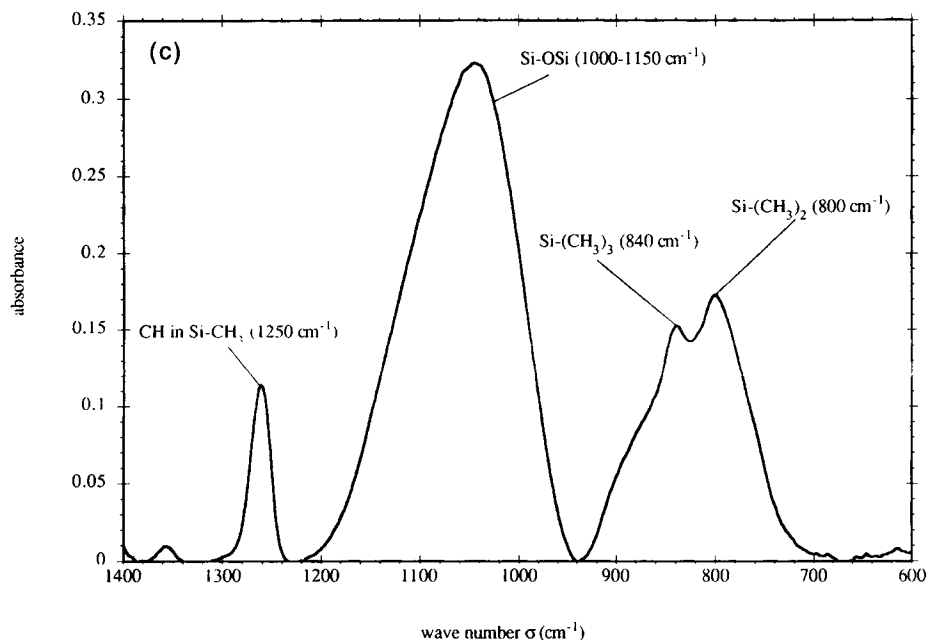
$$P = S \cdot D \qquad (1)$$

Si-OSi (1000-1150 cm⁻¹)

Si-(CH₃)₂ (800 cm⁻¹)

Si-(CH₃)₃ (840 cm⁻¹)

CH in Si-CH₃ (1250 cm⁻¹)

Figure 2   (*Continued from the previous page*)

where S is the solubility factor, and D, the diffusion coefficient.

Let us consider the simplest case of the diffusion process following Fick's law and the gas sorption following Henry's law. The cohesive energy densities (C.E.D) of both, the diffusing molecules and the polymer, control the penetrant sorption at the membrane surface.[17]

The diffusion follows an activation process identical to the sorption. It depends on energy required to create a passage within the polymer permitting the penetrant to migrate from site to site. This explanation is associated with the free-volume theory that leads to the expression of the diffusion coefficient[18,19]:

$$D = A \cdot \exp\left(-\frac{B}{V_f}\right) \qquad (2)$$

where A and B are characteristic constants for a given gas, and V_f, the free-volume fraction inside the material.

In the event of the barrier quality being dependent on the chemical composition, oxygen sorption, controlled by the polymer–penetrant interactions, will be the principal factor affecting the permeability. In that case, the radical content of the plasma films[20] could have an influence on sorption.[7] On the other hand, if the decay in membrane permeability is due to the increase in film density, the preponderant

Table I   Band Assignments of IR Spectra of HMDSO Plasma-deposited Films

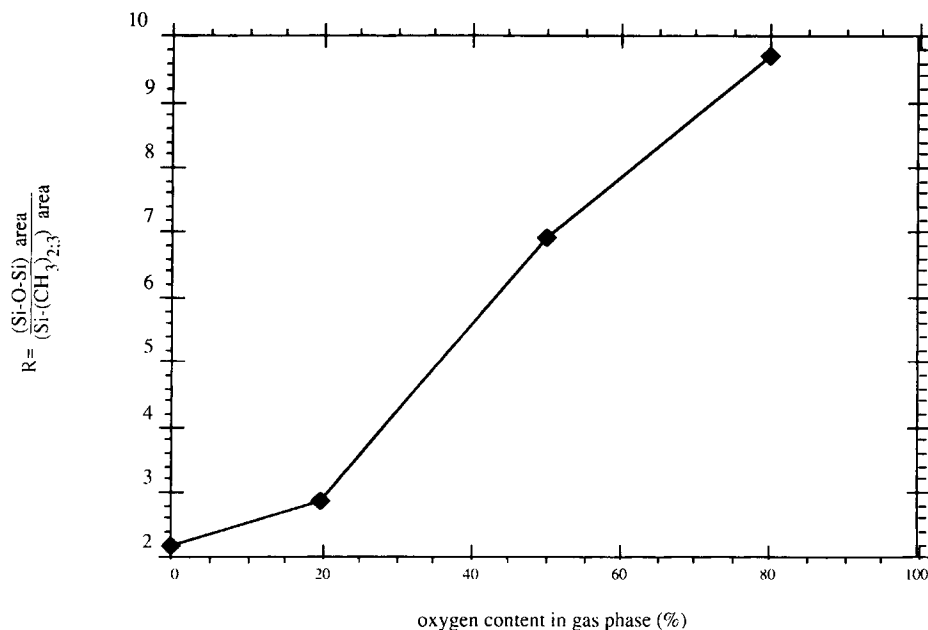| Wavenumber σ (cm⁻¹)	Assignment in Plasma Polymer HMDSO Films	Vibration
2960	C — H in CH₃	Asymmetric stretch
2880	C — H in CH₂	Asymmetric stretch
2150	Si — H	Stretch
1400	C — H in Si — CH₃	Asymmetric bend
1360	C — H in Si — CH₂ — Si	Asymmetric bend
1250	C — H in Si — CH₃	Asymmetric bend
1150–1000	Si — O — Si	Asymmetric stretch
840	Si — (CH₃)₃	Rocking
800	Si — (CH₂)₃	Rocking

Figure 3   Infrared areas ratio of Si — O — Si on Si — CH₃ bonds for different gas-phase compositions. Uncoated polypropylene reference-flow $= 600 \text{ cm}^3/\text{m}^2$ day. Initial gas total pressure $= 10^{-1}$ mbar; power density $= 100 \text{ mW/cm}^2$; deposition time $= 10$ min.

factor will be the diffusion coefficient of the penetrant which depends on the bulk of the deposit. So, if the density increases, the free-volume fraction decreases, and according to eq. (2), the diffusion coefficient will be smaller.

To determine which one of these two processes predominates, three different samples, A, B, and C, were prepared (Fig. 4). Characteristics of these samples are shown in Table III. These multilayer samples are made up of two distinct plasma polymers obtained under very different conditions. The layers labeled X show good barrier properties (3% of reference flux) and are dense (2.7 g/cm³) and mainly inorganic. They were made with 80% of air in the gas phase during deposition. The layers labeled Y were made with pure HMDSO and show poor barrier properties (60% of reference flux) and are less dense (1 g/cm³) and mainly organic.

In sample A, a Y-type film is covered by a few hundred angstroms of X-type film (Fig. 4). In terms of permeability, the barrier efficiency of this multilayer is excellent (see Table III). A second approach is realized with the sample B for which the Y-type film is now the upper one, and the X-type, the lower one. It is assumed that the degree of sorption is different for the above two samples due to the two chemically different upper layers subjected to oxygen. In spite of this difference, results are practically the same for both samples. The first conclusion is that the composition and structure of the surface do not affect the barrier properties. Also, the reduction of the diffusion coefficient through the dense film only curtails the oxygen flow. These results can be qualitatively interpreted based on the principle of membrane series superposition[21] in which the layer having the least permeability con-

Table II   Thickness and Permeability of Several Coatings for Different Oxygen Content in Plasma

	Oxygen Content in Plasma			
	0%	20%	50%	80%
Thickness of deposited coating (nm)	1000	750	150	60
Membrane flow in cm³/m² day	380	200	17	15

Uncoated polypropylene reference flow $= 600 \text{ cm}^3/\text{m}^2$ day. Initial gas total pressure $= 10^{-1}$ mbar; power density $= 100 \text{ mW/cm}^2$; deposition time $= 10$ min.
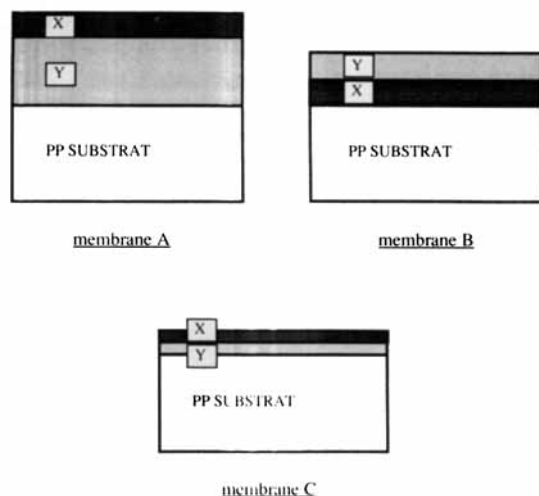
Figure 4 Three models of composite membranes made with two different conditions. Uncoated polypropylene reference flow = 600 cm³/m² day. X layer deposition conditions: 20% HMDSO, 80% air. Nominal oxygen flow = 4% of reference flow. Y layer deposition conditions: 100% HMDSO. Nominal oxygen flow = 60% of reference flow. Substrate: PP 20 μm thickness.

trols the permeability of the overall system. A sorption phenomenon seems not to play a fundamental role in the permeability of plasma polymers. This conclusion is in agreement with observations made on the permeability of conventional polymers subjected to simple gases (oxygen, etc.). In such cases, sorption is controlled mainly by the Lennard-Jones temperature of the gas and is independent of the polymer nature.[22]

At this point it becomes important to determine the minimum thickness of a dense film in order to obtain good barrier properties (typically, a few tenths cm³/m² day). The type C sample is made up of two thin layers: A very thin Y-type layer deposited by a short plasma-pulse (≈ 1 s) in a pure HMDSO gas permits a better adhesion to the polypropylene substrate. Thereafter, another very thin layer (≈ 3 nm) of type X is deposited on the Y type. This membrane remains an efficient barrier exhibiting a permeability slightly higher than in the two previous

cases. We can conclude that the minimum thickness limiting the oxygen flow through the membrane at approximately 3% of the reference value is about 3–5 nm.

Our study shows that the variation of the chemical composition of the plasma polymer is not critical for the membrane permeability to molecular oxygen. Hence, the density of free radicals found in plasma polymers[20] does not change significantly the sorption phenomenon. The film densities are therefore the essential factor limiting oxygen diffusion through the membrane.[6] In fact, a free-volume decrease reduces the diffusion coefficient D and leads to the increase of activation energy of diffusion.[19,23] This assumption is only valid within the framework of the classical theory of solution diffusion related to the permeability of nonpolar small molecules.[8] Moreover, one can suggest that the free-volume magnitude not only determines the diffusion of a penetrant within the plasma polymer, but also affects chain-segment mobility in the polymer matrix.[17,19]

Our results have shown that thicknesses of 5 nm or less provide good barriers to oxygen. It is interesting to compare this result with that of thermally evaporated SiO$_x$ films for which it is reported that about 50 nm are necessary to provide the same barrier quality.[24] This is probably due to a different growth process. In our case, plasma deposition is initiated by an activation of the surface on which radicals coming from a gas phase form a very uniform layer, whereas in evaporation processes, we can expect cluster formations at the surface initially and then a continuous film buildup requiring a thicker layer. This is because the growth rates are, in general, lower for plasma (typically 1 Å/s in our case) compared to evaporation processes.

CONCLUSION

Plasma films from pure HMDSO and HMDSO/O₂ mixtures were deposited on the polypropylene substrate. Depending on the plasma parameters, films

Table III Composition and Permeability of Composite Membranes (Flows are Expressed as Percent of Uncoated Polypropylene Reference Flow = 600 cm³/m² day)

Membrane	Total Deposit Thickness (nm)	Layer X Thickness (nm)	Layer Y Thickness (nm)	O₂ Flux %
A	900	60	840	1.5
B	140	60	80	2
C	≈ 6	3	≈ 3	3.3

of different densities and compositions were obtained. IR spectroscopy was used to check the composition and densities were determined by measuring the thickness and frequency shift of a quartz balance. These results are in good agreement with those previously reported on plasma deposition from pure HMDSO. The barrier efficiency relative to the diffusion of molecular oxygen was measured as a function of thickness and composition of plasma films. It has been shown that oxygen diffusion is largely dependent on the density of films and is not significantly related to the sorption phenomenon. Finally, it was demonstrated that a coating thickness of 5 nm or less is enough to provide a good barrier (20 cm^3/m^2 day, i.e., about 3% of the reference value of the oxygen flow through uncoated films).

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